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A COMPUTER SIMULATION AND PARAMETRIC STUDY
OF A SASOL TYPE FLUIDIZED BED FISCHER-TROPSCH REACTOR

by

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ABSTRACT

Signature_____

A COMPUTER SIMULATION AND PARAMETRIC STUDY OF A SASOL TYPE FLUIDIZED BED FISCHER-TROPSCH REACTOR

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A computer program composed of a mass and energy balance for a Sasol type Fischer-Tropsch fluidized bed reactor is presented. This program is added to a larger existing program which simulates the production of synthesis gas. The synthesis gas produced is based on Williams Fork coal. An equipment cost analysis in 1979 dollars is also included.

A parametric study is performed using temperature, pressure, degree of hydrocarbon saturation and average hydrocarbon chain length as variables. Increasing temperature is found to decrease the amount of hydrocarbons formed. The

1
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results of variation of pressure confirmed a relationship exists between conversion, temperature and residence time. The effect on product distribution by varying the last two parameters is negligible. Relationships between reactor pressure and temperature and the hydrocarbon degree of saturation and average chain length exists, however, at this time only general trends are known.

A summary of the thermodynamics and kinetics of the Fischer-Tropsch reaction is also presented.

DESCRIPTORS

Average chain length

Degree of saturation

Fischer-Tropsch reaction

Pressure effect

Residence time

Selectivity

Conversion

Economic analysis

Fluidized bed reactor

Rate of reaction.

Sasol

Temperature effect

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NOMENCLATURE

A	Arrhenius constant
ALC	Alcohols
a,c,d	Percent of CO converted to product via reaction A, C, D respectively
b	Percent saturation of hydrocarbons by reaction B
CHL1	Chain length of hydrocarbon
CHL2	Chain length of alcohols
CO	Carbon monoxide
CO ₂	Carbon dioxide
Cp	Heat capacity
D	Average degree of polymerization
DNXX	Change in moles of XX
DPXX	Change in pressure of XX
dt	Change in time
E	Activation energy
Fe	Non-oxide catalyst surface
H ₂	Hydrogen
HC, HY	Hydrocarbons
H ₂ O	Water
H ₂ S	Hydrogen sulfide
k	Reaction constant
n	Chain length

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1.0 INTRODUCTION

On Sunday, July 15, 1979, President Carter announced a proposal to start a national synthetic fuel industry. There are many different processes which produce synthetic fuels, the process discussed in this work is coal conversion to a crude oil product via the Fischer-Tropsch process.

The purpose of this work is to simulate the behavior of a Sasol (South African Coal, Oil and Gas Corp., Ltd.) type fluidized bed Fischer-Tropsch reactor through a computer model. This reactor is now part of a larger model simulating a coal gasification process in which the methanation step has been replaced by a Fischer-Tropsch unit. This program includes a mass and energy balance and a cost analysis for a hypothetical plant.

Since the Fischer-Tropsch Process is a very complex one, the exact relationships involving temperature, pressure, product distribution and conversion are not known. Therefore, in order to examine general trends in the behavior of the model, a parametric study was performed. The results of that study are examined here.

2.0 HISTORICAL BACKGROUND

2.1 Discovery of the Fischer-Tropsch Process

In 1902, Sabatier and Senderns demonstrated that CO, CO₂ and H₂ could form methane when reacted over a nickel catalyst. The next advance in CO-H₂ chemistry occurred in 1922, when two German chemists, Franz Fischer and Hans Tropsch, formed oxygenated hydrocarbons over iron turnings. In 1925, Fischer and Tropsch discovered the process now named after them, by forming gasoline and diesel fuel from CO and H₂ over an iron catalyst. Later it was discovered other catalysts such as cobalt, ruthenium, zinc oxide and thorium oxide would also produce hydrocarbons. Each of these catalysts produce different types of hydrocarbons at different operating conditions. For example, zinc oxide produces methanol at 100 atmospheres and 300°C whereas iron oxide catalysts form paraffins, olefins and some alcohols. Ruthenium on the other hand, surpasses all other catalysts in forming high melting ^{par}paraffins. Cobalt forms a product somewhat like that of iron but at lower temperatures and pressures and its product tends to be more paraffinic.

2.2 Early Commercialization

In pre-World War II Germany, 1936-1939, as many as nine Fischer-Tropsch plants produced 740,000 net tons of synthetic fuel in fixed bed reactors using a cobalt catalyst at medium temperatures and pressures. The main purpose of these plants was to supply gasoline and diesel fuel (although some of the product was used as chemical feedstocks). The gasoline produced was of low octane value and had to be up-graded, however, the diesel fuel was of high quality. Towards the end of World War II, when Hitler lost his North African oil fields, these plants helped sustain the German war effort.

In the late 1940's and early 1950's several plants were built in the United States and other countries. These plants were soon shut down because they could not compete economically with cheap oil.

2.3 Modern Commercialization

The single exception to the uneconomical operation of Fischer-Tropsch plants was South Africa. Special incentives and a government-run corporation made it possible to continue to synthetically produce crude oil there. In 1951, M. W. Kellogg Co. was asked by the South Africans to set up a Fischer-Tropsch

plant using both their fluidized bed reactor and the fixed bed reactor of German design. For both types of reactors, an iron oxide type catalyst was used. Included in the Sasol (South African Coal, Oil and Gas Corp., Ltd.) project was a new town, coal mine, synthesis gas plant and a refinery. Initially, this plant supplied twenty percent of South Africa's motor fuel needs.

In 1973-74 the Arab oil embargo made the Sasol plant more economical. This situation combined with the Organization of Petroleum Exporting Countries' unwillingness to sell South Africa oil made it necessary for South Africa to find other sources of oil. In 1976, South Africa announced it was building Sasol II, a 2.3 billion dollar synthetic fuel plant, followed by a 3.8 billion dollar expansion of that plant. It is expected this massive new plant will be on stream in 1981. The combined capacity of these Fischer-Tropsch plants should provide fifty percent of South Africa's motor fuel needs. Also, Sasol has just announced the sale of its proprietary knowledge of the process as of September 1979.

The Fischer-Tropsch process is an old process which has been around for a long time and will probably be an important link in supplying our future energy needs.

3.0 THEORETICAL BACKGROUND

In this section, a brief review of the Fischer-Tropsch chemistry in terms of thermodynamic equilibrium, kinetic mechanism and rates of reaction will be given. Since most Fischer-Tropsch processes are operated far from equilibrium, the thermodynamics can only offer guidelines as to the feasibility of certain reactions occurring at operating conditions. The mechanism can lead to an understanding of the kinetics involved. The rates of reaction hold the most important role, because they determine actual product formation and distribution. The following general reaction shows the reactants and products involved in the Fischer-Tropsch reaction.

The general reaction may be expressed as,

3.1 Thermodynamics

Comparing the Gibbs Free Energy of formation for each compound against another on a per carbon atom basis, the compound with the most negative Gibbs Free Energy is the most

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stable one.^{(1)*} For a given chain length and a temperature range of 300-800K, the order of stability for alkanes, alkenes, and alcohols is

alkanes > alkenes > alcohols

For temperatures above 500-600K and a chain length greater than six, alkylbenzenes are preferred.

The most favored product as a function of chain length changes with the class of compound. For alkanes the preferred product is the one with the least carbon number, i.e. methane. This trend is independent of temperature. For alkenes the trend is to favor the one with the largest carbon number. However, this trend reverses itself at 500-750K and one atmosphere, under which lighter alkenes are preferred. Alkylbenzenes follow the behavior of the alkene with a reversal occurring at 600K. For alcohols the equilibrium tends to favor longer chain lengths regardless of temperature.

Finally, the free energies increase with temperature and become positive at sufficiently high temperatures. The temperature at which this occurs for each class of compound

*Parenthetical references placed superior to the line of text refer to the bibliography.

is shown below:

alkanes	$T > 650K$
alkenes	$T \sim 650K$
alcohols	$T > 400K$
alkylbenzenes	$T \sim 700K$

Thus, it is clear at all temperatures methane is the most stable compound and so always preferred since at higher temperatures the product tends to have a shorter average chain length.⁽²⁾

3.2 Mechanism

Ever since the Fischer-Tropsch chemistry was discovered, many different mechanisms have been proposed. The difference in most of these mechanisms seems to lie in how the oxygen atom is removed from the adsorbed carbon monoxide molecule. The majority of these mechanisms agree on the stepwise growth of an adsorbed hydrocarbon complex. One accepted mechanism is that of Eidus⁽¹⁾ which is outlined below. This mechanism seems to be the basis of Dry's equation for determining the rate of reaction.⁽²⁾

Formation of Hydroxyl Carbon and Reduction

Polymerization,

Desorption (chain termination),

The formation of oxygenated compounds is thought to follow the following route.

Typical Oxygenate Formation

The above mechanism implies the following behavior:

(A) the rate determining step is the addition of hydrogen to the CO bond;

(B) the hydroxy carbene is rapidly hydrogenated to form methane and higher hydrocarbons;

(C) similar mechanisms appear to apply to methane and higher hydrocarbons;

(D) the production of olefins and oxygenated intermediates probably proceeds by alternation of the desorption step to form unsaturated species or to incorporate CO for oxygenated species.

The above mechanism illustrates the importance which the partial pressures of CO and H₂ play in determining the rate of reaction involved in Fischer-Tropsch chemistry. The kinetics

of this reaction, which occurs simultaneously with the Water Gas Shift reaction, is examined in the next section.

3.3 Kinetics

The kinetic rates for both the Fischer-Tropsch and the Water^{gas} Shift reaction are discussed here along with the factors affecting catalyst poisoning and product distribution.

3.3.1 Rate of Reaction

At very low partial pressures of CO ($< 10^{-2}$ atm) and higher partial pressure of H₂ (1 atm) the following kinetic expression is observed.⁽¹⁾

$$r_{HC} = k P_{H_2}^0 P_{CO}^{-1} \quad (3-8)$$

where k is the rate constant, r_{HC} is the rate of hydrocarbon formation, P_{CO} is the partial pressure of CO and P_{H_2} is the partial pressure of H₂. However, as the CO pressure increases, the observed kinetics change so that the CO dependence becomes approximately zero order and the H₂ dependence increases to first order.⁽¹⁾ The change in CO dependence can be understood as the eventual saturation of the catalyst surface by CO. The H₂ dependence changes because the H₂ weakens the C-O bond strength and causes the hydroxy carbene formation. This gives

the rate equation a positive H_2 dependence.

Dry of the Sasol company has developed the following expression for the rate of reaction. (2)

$$r_{HC} \text{ (rate of reaction)} = Ae^{(-E/RT)} \frac{P_{CO} P_{H_2}}{(P_{CO} + \alpha P_{H_2O})} \quad (3-9)$$

where α is the relative rate of physical adsorption of water over the chemisorption of CO, A is the Arrhenius constant (sec^{-1}) and E is the activation energy for a high temperature fluidized bed (6 Kcal/mole). The temperature T is in degrees Kelvin and P_{CO} , P_{H_2} , P_{H_2O} are the partial pressures of carbon dioxide, hydrogen, and water, respectively.

The water gas shift reaction occurs simultaneously with the Fischer-Tropsch reaction. The water gas shift reaction is generally assumed to be at equilibrium throughout the length of the reactor, (2) and the following rates of reaction were found to describe the water gas shift reaction in equilibrium for a Fe_2O_3 catalyst. (3)

Water Gas Shift Reaction

$$r_1 = A_1 e^{(-E_1/RT)} P_{CO} (P_{H_2O}/P_{H_2})^{.5} \quad (3-11)$$

$$r_2 = A_2 e^{(-E_2/RT)} P_{CO_2} (P_{H_2}/P_{H_2O})^{.5} \quad (3-12)$$

The forward reaction forms CO_2 and H_2 while the reverse reaction forms CO and water.

The selectivity of the catalyst to form products other than methane is controlled by several important considerations. The first of these is the degree of alkalinity of the catalyst. The Sasol catalyst is Fe_3O_4 promoted with K_2O , MgO and Al_3O_4 .^(1,4) The group I alkali, K_2O enhances the selectivity of the catalyst by reacting with the silica in the gas phase to form less basic silicates.⁽²⁾ The MgO and Al_3O_4 are important in increasing the surface area of the catalyst and thus its activity.^(1,4) Dry has shown the most important parameter in increasing the selectivity of the catalyst to heavy ends to be the basicity of the catalyst.⁽²⁾ The second most important factor influencing the selectivity of the catalyst is the partial pressure of CO_2 . As the partial pressure of CO_2 rises the product distribution increases in heavy ends such as gasoline and diesel fuel. Dry shows this to be true even when the H_2/CO ratio is increased.⁽²⁾ However, the effect of

*Temp
to
high*

CO_2 is not as pronounced when a catalyst of high basicity is used. Since an increase in reactor pressure will increase the partial pressure of CO_2 , at higher reactor pressures a greater amount of heavy ends are produced. (2)

The poisoning of the catalyst occurs mainly through carbon deposition on the catalyst surfaces. The rate of carbon deposition is influenced by three factors: temperature, basicity of the catalyst and the $P_{\text{CO}}/P_{\text{H}_2}^3$ ratio in the reactor. (2)

When the basicity of the catalyst is increased, the carbon deposition rate first decreases and then increases. As the ratio of partial pressures, $P_{\text{CO}}/P_{\text{H}_2}^3$, is increased the carbon deposition rate increases. Because of the nature of this parameter, if all other reactor parameters are kept constant, the higher the reactor pressure, the lower the carbon deposition rate will be. (2) (2)

An added advantage is that it gives a faster throughput when the reactor is operated under higher pressure. (2)

A parameter of secondary importance is that of temperature. The effect of rising temperature increases the production of light hydrocarbons, olefins and aromatics. However, an accurate determination of this effect is hampered by insufficient data. (2)

Finally, many years of operating experience have shown that the residence time of the gases in the reactor affect the

2
degree of olefinity and the amount of oxygenated compounds produced. (2) In fact, the product is much more olefinic and oxygenated than predicted by the thermodynamics. This shows that it is kinetic considerations, not thermodynamic ones, which have the most influence over product distribution.

3.3.2 The Schultz-Flory Theory of Most Probable Distribution

At present, one of the promising theories for predicting product distribution is that proposed by the Schultz-Flory Theory based on the following assumptions. (1,2)

(A) A constant number of active polymerization sites equal to some function of active catalytic surface sites are maintained. This arises from the fact chain termination occurs by desorption of the molecule from the surface and new chains can be started.

(B) All hydrocarbon species on the surface have an equal probability of adding a carbon and forming molecule one carbon longer.

Schultz and Flory have developed the following expression linking the weight fraction (W_n) for a molecule of chain length (n) with the probability (p) that each carbon is polymerized.

$$W_n = n \cdot (1-p)^2 \cdot p^{n-1} \quad (3-13)$$

or

$$\log \left(\frac{W_n}{n} \right) = n \log p + \log \left(\frac{1-p}{p} \right)^2 \quad (3-13a)$$

The average degree of polymerization or average chain length (D) is a function of the probability (p),

$$D = \frac{1}{(1-p)}$$

The average chain length of the product is easier to comprehend and has been used in Figure 1, ⁽¹⁾ where it is used to calculate the product distribution in fractions of petrochemical interest.

3.3.3 Summary of the Thermodynamic and Kinetic Constraints of Fischer-Tropsch Chemistry

(A) Methane is the ^{*predominant*} preferred product at all temperatures and pressures;

(B) More complex hydrocarbons such as aromatics and olefins are thermodynamically favored over paraffins only at high temperatures;

(C) Increasing temperature significantly decreases the driving force of hydrocarbon synthesis from CO and H₂ and therefore, require high pressure to overcome equilibrium limitations; ⁽⁴⁾

FIGURE 1: Variation of Typical Product Split with Degree of Polymerization⁽¹⁾

(D) In a fluidized bed, although olefins and oxygenated compounds are thermodynamically unstable, they appear in appreciable quantities. This suggests primary products and the degree to which they emerge from reactors is dependent upon the residence times within the catalyst particles and the degree of hydrogenation possible; ⁽²⁾

(E) Catalyst selectivity is primarily controlled by the reaction mechanism; (3)

(F) Existing evidences show that in the Fischer-Tropsch process, the Schultz-Flory kinetic theory is obeyed. ^(1,2)

4.0 COMPUTER PROGRAM

This section is composed of two parts, the first describes the Fischer-Tropsch subprogram and the second describes the Synthane computer program to which Fischer-Tropsch program was added.

4.1 Fischer-Tropsch Reactor Model

4.1.1 Basic Description of the Reactor

The Fischer-Tropsch reactor is based on the description of a Sasol reactor given in the literature.^(2,5) This reactor is approximately thirty-nine meters high and three meters in diameter. It contains 200 to 300 tons of iron oxide catalyst and approximately one-fourth of its volume is used for cooling coils. Through the cooling coils oil is pumped for heat removal. The hot oil is used to heat up the incoming synthesis gas to 150°C. The feed gas reacts with the circulating hot iron oxide catalyst. After exiting the reactor, the iron catalyst/vapor mixture enters a catalyst hopper containing cyclones for separation of the catalyst from product gas. The catalyst then continues through the hopper and is again added to the feed gas stream on its way to the reactor. This

FIGURE 2: Flowsheet of Medium-Pressure Synthesis on Iron Catalyst with Entrained, Fluid-Bed Reactor⁽⁴⁾

compares with the Sasol reactor which has a 2/1 recycle ratio of reformed tail gas to feed gas entering the reactor. The Sasol plant also has a product gas clean up and a refinery downstream.

4.1.2 Fischer-Tropsch Reactor Mass and Energy Balance

In order to simulate the Fischer-Tropsch reactor, the mass and energy balances are needed. The mass balance (in this case a mole balance) is based on the following stoichiometric equations. (1,4)

Reaction

where n is the average chain length of the hydrocarbons and n_A is the average chain length of the alcohols. Equation (4-4) is the Water Gas Shift reaction. From these equations the following mole balances are made for the change in moles via reaction A, B, C, or D. The change in moles of CO is used as a basis and a , c , or d are the percentage of CO involved in

reaction A, C, or D respectively. The value of b is the assumed percentage of saturated hydrocarbons.

$$\text{DNCO} = (a + c + d) \text{ DNCO} \quad (4-5)$$

or

$$a + c + d = 1.0 \quad (4-5a)$$

$$\text{DNHY} = (-.5a) \text{ DNCO}/n \quad (4-6)$$

$$\text{DNH}_2 = (.5a + 2c - d) \text{ DNCO} - b \text{ DNHY} \quad (4-7)$$

$$\text{DNAL} = - .0751/n_A \text{ DNCO} \quad (4-8)$$

$$\text{DNCO}_2 = (-.5a - d) \text{ DNCO} \quad (4-9)$$

$$\text{DNH}_2\text{O} = \left(- \left(\frac{n_A - 1}{n_A}\right) c + d\right) \text{ DNCO} \quad (4-10)$$

where DNCO, DNHY, DNH_2 , DNAL, DNCO_2 and DNH_2O are the disappearance or appearance of CO, hydrocarbons, H_2 , alcohols, CO_2 and H_2O .

These equations are compared with the following rate of reaction equations from the section on theory.

Water Gas Shift

$$r_A = k_A P_{\text{CO}} (P_{\text{H}_2\text{O}}/P_{\text{H}_2})^{.5} \quad (4-11)$$

$$r_B = k_B P_{\text{CO}_2} (P_{\text{H}_2}/P_{\text{H}_2\text{O}})^{.5} \quad (4-12)$$

Fischer-Tropsch Hydrocarbons

$$r_{\text{HC}} = k_{\text{HC}} \frac{P_{\text{H}_2} P_{\text{CO}}}{(P_{\text{CO}} + cP_{\text{H}_2\text{O}})} \quad (4-13)$$

Fischer-Tropsch Alcohols

$$r_{\text{ALC}} = -0.0751 DP_{\text{CO}}/n_A \quad (4-14)$$

This is based on the assumption that 7.51 mole % of CO is converted to alcohols. (In other words, a fixed value of c was assumed.)

These equations are combined to find the change in the partial pressures of CO and hydrocarbons shown below.

$$-r_{\text{CO}} = -\frac{dP_{\text{CO}}}{dt} = r_A - r_B + r_{\text{HC}} + r_{\text{ALC}} \quad (4-15)$$

and

$$r_{HC} = \frac{dp_{HC}}{dt} \quad (4-16)$$

The algorithm for finding the change in moles involves the following steps:

(A) the rates of reaction are calculated using the initial feed stream partial pressures;

(B) therefore, a change in partial pressures of CO and hydrocarbons with time can be found;

(C) a small incremental change in the partial pressure of CO is assumed to find the change in time;

(D) the time increment is then used in equation (4-16) so that the change in the partial pressure of hydrocarbons is found;

(E) the partial pressures in the feed gas stream and the change in partial pressures for CO and the hydrocarbons are converted to moles via the ideal gas law by assuming the total pressure and temperature are constant;

(F) the value of (a) is found by rearranging equation (4-6) and the knowing the values of DNCO and DNHY previously calculated;

(G) the value of d can be found by equation (4-5a);

(H) a value of c is assumed, then the rest of the changes in moles for the other species present can be calculated;

(I) the calculation is continued by assuming the new molar values for the new time period which are found for each species by equating them to their original values plus the change in moles over the time increment;

(J) the new partial pressures are found by using the ideal gas law again;

(K) the algorithm then goes back to the first step and continues to repeat itself until the assumed overall conversion of CO is reached;

(L) then the composition of the final product is printed out.

During the computation the residence time (τ) is also being calculated by the following equation

$$\tau = \int_{P_{CO \text{ initial}}}^{P_{CO \text{ final}}} \frac{dP_{CO}}{-r_{CO}} \quad (4-17)$$

The calculation is done numerically using the trapezoidal rule integration method. A scale up factor is also calculated so

that a product rate equivalent to a heating value of 2.42 billion KCal per hour* is produced.

Once the mass balance is completed, the energy balance is made by finding the change in enthalpies of the entering and exiting streams concerned. This is done for the reactor, oil and water cooling streams. The mass and energy balances, as part of the computer program are shown in Appendix A.

4.1.3 Fischer-Tropsch Reactor Unit Economics

The economic portion of this program estimates the costs for the feed gas-oil heat exchanger, the Fischer-Tropsch reactor, the oil cooler, a start-up heater, an oil pump, and a waste water pump. Before any costs can be estimated, the plant has to be scaled up in the size subroutine. In this subroutine all flow rates or rates of heat removal calculated by the mass and energy balance are multiplied by the scale factor and converted to their proper units. Using this size subroutine, (shown in Appendix B), the costs of the Fischer-Tropsch unit can be calculated. These costs are in 1979 dollars

*This is equivalent to a coal gasification plant producing $6.68 \times 10^6 \text{ Nm}^3$ of high Btu gas.

representing equipment and catalyst costs. Only for the Fischer-Tropsch reactor and the catalyst hopper did a new calculation sequence have to be found. All other costs for units such as pumps and heat exchangers could be calculated using subroutines already a part of the Synthane program. The reactor vessel costs was calculated by finding how much steel was needed, finding the cost of the steel and multiplying by four to find its fabrication cost. The cost of the catalyst hopper vessel was assumed to be the same as the Fischer-Tropsch reactor. The cost of the Fischer-Tropsch reactor vessel was then added to the cost of the cooling coils inside (this cost was found by a method used for the methanator in the synthane program). For the catalyst hopper the cost of the cyclone (calculated by an existing subroutine) to the cost of the vessel. The Fischer-Tropsch costing subroutine is found in Appendix C.

4.1.4 Assumptions

The following assumptions have been made:

- (A) the reactor temperature and pressure are assumed constant;
- (B) the ideal gas law is assumed to be a good approximation;

(C) the feed gas is assumed to enter the reactor at 150°C;

(D) the percentage of CO reacted to form alcohols is assumed to be 7.51;

(E) a basis of product rate equivalent to 2.42 billion KCal per hour heating value is assumed;

(F) no carbon deposition rate on the catalyst is assumed;

(G) the heat capacity of hydrocarbons and alcohols was assumed to follow the equation shown below.

$$C_p = (3(N) - 3/2) \times R \quad (4-18)$$

where N is the chain length and R is the ideal gas constant;

longer
(H) the residence time is assumed to be five times faster than that calculated by equation (4-17) due to the fact the rate equations are based on a Fe_2O_3 catalyst instead of a Fe_3O_4 catalyst.

4.1.5 Correlation

Only one correlation was used in this program and that is to find the average chain length of alcohols from the average chain length of hydrocarbons. Since it is assumed that a hydrocarbon chain length of one the alcohol chain length must

also be one and it was calculated from the product distribution given in the literature that at an average hydrocarbon chain length of 3.25, the alcohol average chain length is 2.5. By assuming a linear dependence on the hydrocarbon chain length (CHL1) the following equation finds the alcohol chain length (CHL2).

$$\text{CHL2} = (.3333 + .6667 * \text{CHL1})$$

4.1.6 Input Variables

For the Fischer-Tropsch subroutine the following variables can be read.

TFT	reactor operating temperature in degrees rankine
PFT	reactor total pressure in pounds per square inch absolute
CONVCO	overall conversion of CO
F	the percent of hydrocarbons which are saturated
CHL	average chain length of the hydrocarbons
HHYC	enthalpy of a fictional average chain length hydrocarbon at 25°C. Example, if the average chain length is 3, find the enthalpy of propane.
HALC	enthalpy of a fictional average chain length alcohol at 25°C

HTVAL1 heat of combustion of fictional average chain
 length hydrocarbon at standard conditions

HTVAL2 same as HTVAL1 except for alcohol

4.2 The Synthane Process Computer Program

The Synthane process is an experimental process whereby coal can be gasified to form synthetic natural gas. The developmental work has been sponsored by the U.S. government and this program is a result of some of that work. The mass balances are made by correlating feed coal composition, operating conditions and other variables with the product gas composition. The program consists of a number of subroutines which can be used separately. These subroutines are of three basic types. The first type subroutine is the one which does the mass and energy balance for a process stream through a piece of equipment. Each major category of equipment, such as coal preparation, gasification dust and tar removal, shift conversion, waste heat recovery and gas purification, have a subroutine. The final unit here is the Fischer-Tropsch reactor which replaces the methanation step. There is also a sizing subroutine which increases the flow rates of the process streams so that a 9.64 billion Btu/hour product stream is obtained. Finally, the equipment costs are calculated and the total

capital cost, including overhead, is obtained.

The input variables for the Synthane process are found in the program manual of the Synthane program.⁽⁶⁾

5.0 PARAMETRIC STUDY: DISCUSSION OF RESULTS

A parametric study is carried out to examine the effect of several important process variables, these include temperature, pressure, average chain length and, finally, percentage of total saturated product. The feed gas composition was held constant for each run as was its incoming temperature before mixing with the catalyst. The feed gas composition and temperature, based on William Forks coal, are shown below in Table 5.1.

TABLE 5.1

<u>Component</u>	<u>Feed Gas Distribution</u> <u>Mole %</u>
H ₂	73.3
CO	22.9
CO ₂	2.0
Hydrocarbons	0.8
Alcohols	0.0
H ₂ S	0.0
N ₂	0.8
H ₂ O	0.1

The proposed plant is based on a clean product having a heating value of 2.42 billion Kcal an hour. Since the initial calculations of product are based on a 454 Kg coal per day, they must be scaled up to the above flow rate. At different process conditions the product composition changes and so the scale factors also change.

5.1 Variation of Operating Temperature

The temperatures chosen carefully so that they would be close to the temperature range used to determine the Fischer-Tropsch rate of reaction expression by Dry. The results of varying the temperature while holding the other parameters constant is presented in Table 5.2.

As the operating temperature is increased several trends can be seen from Table 5.2. First, as the temperature is increased the conversion of synthesis gas to hydrocarbons decreases, just as the thermodynamics predicted. In the theory section it was stated for increasing temperatures, an increase in total pressure will be needed because of a shift in equilibrium for the Fischer-Tropsch reaction. Another interesting trend is seen in the shift from production of water to hydrogen at higher temperatures. This trend might be attributed to the change in the relative rates of the Fischer-Tropsch to that of

TABLE 5.2

	Temperature (K)		
	500	603	700
Residence Time (sec)	32.34	4.59	1.53
Product Distribution (mole fraction)			
H ₂	.04	.30	.46
CO	.01	.01	.01
CO ₂	.04	.00	.05
Hydrocarbon	.18	.15	.11
Alcohol	.07	.01	.01
N ₂	.02	.01	.01
H ₂ O	.70	.51	.34
Costs and Number of Reactors (millions of dollars)			
Number of Reactors	13	3	2
Cost/Reactor	4.15	7.35	9.52
Total Cost	76.00	34.9	30.6

the Water Gas Shift Reactions. Another important trend is a decrease in residence time as the temperature is increased. This is what would be expected since higher temperatures lead to larger rates of reaction and thus less time is required for reaction. This behavior also agrees with the thermodynamics and the experience of Dry, which point out higher temperatures and the resulting shorter residence times, lead to greater olefin production.⁽²⁾

Finally as the temperature is increased the cost of the Fischer-Tropsch unit decreases. This occurs because at higher temperatures fewer reactors are required. However, when one compares the decrease in cost of the reactor unit and the decrease in the amount of hydrocarbons produced one sees this decrease in about the proportion. Thus, the unit cost per hydrocarbon remains approximately the same.

5.2 Variation of Operating Pressure

The results of increasing pressure are small. The product distribution, scale factor, and residence times remained constant and the only important parameter to change is the number of reactors. The number of reactors decreased because at higher pressures the volumetric flow rate decreased

and with a constant residence time this lead to a greater overall reactor volume needed for the plant. This result is consistent with the theory which says higher pressures should lead to greater conversion for a given temperature. This statement assumes a constant volume. So for a constant reactor volume increasing pressures will lead to smaller volumetric flow rates, therefore longer residence times, and thus, a higher conversion. This relationship is evidenced in Equation 5-1 taken from Pichler.⁽⁴⁾

$$\ln (1-x) = k (\tau) \quad (5-1)$$

where x is percent conversion of CO and H_2 , k is the rate constant and τ is the residence time. Even though this relationship was probably developed for a fixed bed reactor, it does provide an indication that if the percent conversion and temperature (and thus the rate constant) are fixed, the residence time will be also.

As stated in the theoretical section, higher pressures do affect the catalyst selectivity in favor of longer chain lengths and slower carbon deposition rates. However, correlations linking these effects to higher pressures are not known at this time.

5.3 Variation of the Degree of Saturation

Although it is known that the percentage of saturated hydrocarbon production decreases with increasing temperature, there is not enough data in the literature to formulate a correlation. The percentage of saturated hydrocarbons, of course, can never exceed 100 or be less than zero. The results of the variation of this parameter (while holding the other parameters constant) is shown below.

TABLE 5.4

	Percent Saturated		
	.25	.50	.75
Residence time (sec)	4.587	4.589	4.598
Product Distribution (mole Percent)			
H ₂	12.13	11.05	11.19
CO	.47	.49	.51
Hydrocarbons	5.69	5.61	5.53
Alcohols	20.13	19.61	19.14
Cost and Number of Reactors (millions of dollars)			
Number of reactors	3	3	3
Cost/Reactor	7.42	7.35	7.28
Cost of F-T unit	35.31	34.96	34.65
Scale factor	1128	1149	1168

The effect of increasing the percentage of saturated hydrocarbons on residence time, product distribution and the cost were slight. However, an increase in saturation does lead to a slightly higher residence time just as Dry suggested.⁽²⁾ When the number of moles of hydrogen and water are added, their sum decreases with increasing saturation. This indicates at higher saturation less hydrogen is available for the water gas shift reaction and more is included in the hydrocarbons.

The scale factor increases due to a decrease in both the hydrocarbon and hydrogen content of the product stream with increasing product saturation.

5.4 Variation with Chain Length

The final parameter to be varied is the average hydrocarbon chain length. A wide range of chain lengths were used to exaggerate any differences in computer run results. These results are presented below.

TABLE 5.5

	Average Chain Length			
	2.5	3.25	5.0	10.0
Residence time (sec)	4.89	4.59	4.10	3.13
Product Distribution (mole fraction)				
H ₂	0.37	0.30	0.19	0.08
CO	0.01	0.01	0.01	0.01
CO ₂	0.02	0.00	0.00	0.04
Hydrocarbon	0.16	0.15	0.12	0.07
Alcohol	0.01	0.01	0.01	0.00
N ₂	0.01	0.01	0.02	0.02
H ₂ O	0.41	0.52	0.05	0.77
Cost and Number of Reactors (millions of dollars)				
Number of Reactors	3	3	3	3
Cost/Reactor	7.086	7.35	9.46	10.61
Cost of Fischer-Tropsch Unit	33.58	34.96	44.3	51.18

As the chain length increases the trend of the residence time is to decrease slightly. It is hard to examine the importance of this trend all by itself since the chain length and residence time are very much a function of catalyst composition and the operating temperature. As the chain length increases, the mole percentage of the hydrocarbons declines just as one would expect since the average molecular weight is increasing.

The cost of the Fischer-Tropsch reactors increase with increasing chain length and this occurs because the scale factor increases. The scale factor increases because as the chain length increases a shift from hydrogen to water production occurs.

6.0 CONCLUSIONS

Based on the results of the present study, the following conclusions can be made.

(A) The calculated results successfully illustrate the temperature dependence of the conversion of CO and H₂ to hydrocarbons. At lower temperatures more hydrocarbons were produced.

(B) The results of the variation of the reactor pressure confirmed a relationship between conversion, residence time and temperature exists.

(C) The only real effect in increasing the degree of saturation of hydrocarbon was a slight increase in residence time.

(D) Longer chain lengths were found to correspond to a decrease in residence times.

(E) The cost of reactor units decreased with increasing temperature and degree of saturation, but increased with increasing chain length.

Finally, several recommendations are suggested for improving the program.

(A) Although the Synthane process is a good one, further modifications are required to simulate the Sasol process upstream from the Fischer-Tropsch Reactor.

(B) A methane reformer could be added to the Fischer-Tropsch Reactor unit so a 2/1 recycle ratio of tail gas to feed gas can be used. This model would more closely simulate the Sasol reactor.

(C) To complete the simulation of a Sasol plant, a refinery model should be added to the present program.

(D) A better economic analysis could be made by including a discounted cash flow type calculation to determine a return on investment. Various types of product distributions could be tried so as to maximize the profitability of a hypothetical plant.

(E) Basic kinetic data is lacking and this information is urgently needed for future design and simulation studies.

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APPENDIX A

MASS AND ENERGY BALANCES

In this appendix, the mass and energy balance subroutine for the Fischer-Tropsch unit is presented. With this new subroutine, several new data cards had to be added to the previously existing Synthane data deck. Their place in the data deck is shown.

The order of the Synthane data cards is given in the Synthane program manual.⁽⁶⁾ The new data cards are interfaced into that order in the following way.

Synthane Card No.	Variable Name	Format
7	Pressure Card	(2F10.0,2F10.8)
New Card 1	TFT PFT F CONVCO	
New Card 2	CHL HHYC HALC	(8F10.8)
8	Coal Preparation Card	

The final card comes just before the numbers of equipment card for the coal preparation step. These cards are not shown in the program manual.

New Card 3	HTVAL1 HTVAL2	(8F10.0)
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OL EN

The following list gives the definitions of important variables in the mass balance.

DYMOLE(J) - change in moles for component j

DPCO,DPCOL - change in partial pressure of CO and previous value of DPCO, respectively

DT - change in time

P(J) - partial pressure of component J

PCOI - initial partial pressure of CO in feed gas

SCAL - scale factor of plant

STPV - volumetric flow rate of product (standard conditions)

VDOT - volumetric flow rate

YCOEND - number of moles of CO out of reactor for assumed conversion, CONVCO

YLMOLE(J) - moles of component J

Y8(J) - initial molar value of component J in feed gas

J = 1 - H₂

2 - CO

3 - CO₂

4 - H₂C

5 - ALC

6 - H₂S

7 - N₂

8 - H₂O

The following Figure (A-1) shows the major variables involved in the energy balance.

FIGURE A-1: Block Diagram of Fischer-Tropsch Unit

DHOIL, DH9A, DH8A - Heat entering or leaving streams

TCW, TCWS, TOI, TOL, T_{m2} , T_{m3} , T_{m4} , T_{m5} , Temp - temperature of stream

HOILIN, HOLV, OILV3 - Enthalpy of oil streams

MASS AND ENERGY BALANCES

```

SUBROUTINE FISCHT
C
C THIS SUBROUTINE DOES MASS AND ENERGY BALANCES FOR FISCHER-
C TROPSCH REACTOR (SASOL FLUIDIZED BED TYPE)
C
COMMON /C1/ YIMOLE(4),WTP1(8),WTPRP1(8),Y1(8),P1,MIP,NP1
COMMON /C5/ COMP(6,5),MOLWT(6,5)
COMMON /C7/ TPTF1
COMMON /F11/ FHT,PFT,F,CONVCO
COMMON /F2/ CHL,HEYC,HALC
COMMON /CP/ SCAL,FEED,PAIPAH,HICPAH,SICPAH,HICPEH,SICPEH,TSCP,
SAIRMP,TOTDUT,FICI
COMMON /F3/ HILR,DEQA,DH01L,VDOTL,VDOTI,UMOLE,GW1,TOL,
ITEMP,OTCX
COMMON /TEMP/ TCW,TCWS,TCPAH1,TCPAH2,TCPAH3,TCPAH4,TCPRH1,TCPRH2,
TCPRH3,TCPRH4,TGF1,TGF2,TGF3,TGF4,TGP2,TGP3,TLPS,TSCP1,TSC1,TSC2,
TOP3,TSE1,TSE2,TWER1,TRH1,TEGC1,TA1,TCGC1,TRG1,TRG2,IM2,IM3,TMS,
THPS
COMMON /PRSUM/ PGI,PSC1,PAHP1,PRB1,PEGC1,PAHS,PCGC1,PM1
COMMON /WAT1/ SFTOTW,SECONW,WHRCOND,PRCOND,FGCOND,AMSCND,ARSDU,CGCKU
1,MTHCND,SPFRC,CHARG
DIMENSION Y10(8),YH(8),Y9A(5),Y8B(8),Y9A(8),Y9B(8),Y9C(8),BTUHA(8)
1,BTUBH(8),BTU9A(8),BTU9B(8),BTU9C(8),P(8),DYMOLE(8)
DIMENSION H1PFT(8),STOV(8),HTVAL(8)
REAL MIP,N
READ(5,8000)HTVAL1,HTVAL2
8000 FORMAT(2F10,2)
COMP(2,4)=IHYC
COMP(2,5)=IALC
MOLWT(2,4)=CHL*14+H*2
MOLWT(2,5)=(.3333+.6667*CHL)*14+18
SUMZ=0
YIMOLE(4)=YIMOLE(4)+YIMOLE(5)
YIMOLE(5)=0
Y1(4)=Y1(4)+Y1(5)
Y1(5)=0
DO 5 J=1,NP1
5 YH(J)=YIMOLE(J)
TP=FHT+46.0
T=TR/1.8
VDUT=P1*10.73*TR/PFT
VDOTI=VDUT/3600
N=CHL
DPCO=-1.
DPCOL=DPCO
DNCOI=YIMOLE(2)
C
C FIND THE PARTIAL PRESSURES
DO 10 J=1,NP1
10 P(J)=PFT*Y1(J)
PCOI=P(2)
YCUEND=(1-CONVCO)*YIMOLE(2)
C
C WRITE INITIAL VALUES
WRITE(6,100)
100 FORMAT(1H1)
WRITE(6,101)
101 FORMAT(30X,'MASS BALANCE FOR THE FISCHER-TROPSCH REACTOR'
1//)

```

```

      NOMP=1
      NOMP=1
      WRITE(6,140)NOMP,NOMP
140  FORMAT(5X,'NUMBER OF FEED STREAMS',4X,'=',14/5X,'NUMBER
      1 OF PRODUCT STREAMS',1X,'=',14)
      WRITE(6,141)NP1,NP1
141  FORMAT(5X,'NUMBER OF COMPONENTS IN FEED STREAM IS',14/5X,
      1'NUMBER OF COMPONENTS IN PRODUCT STREAM IS',14)
      WRITE(6,150)
150  FORMAT(//10X,'GAS PRODUCT STREAM//')
151  FORMAT(12X,'MOLE %',3X,'MOLE %',4X,'MOLES',6X,'WEIGHT',5X,
      1'PRESSURE',1X,'VOLUME',1/12X,'WT.',1,47X,'(1000SCF)')/1)
152  FORMAT(6X,A4,2X,12,5X,PS,2,2(5X,PC,2),5X,F7.3,5X,F7.3)

```

```

C
C
C      FIND THE CHANGE IN MOLES DUE TO RXN
C
20  IF(DPCO .LE. DPCHO)SUMZ=SUMZ+.5*Z
      IF(DPCO .GE. DPCHO)SUMZ=SUMZ-.5*DPCHO/R
      IF(P(R) .EQ. 0)P(R)=.001
      A=2.387E+06*EXP(-8138.17/T)*P(2)*(P(R)/P(1))**.5
      B=7.202E+08*EXP(-12835.3/T)*P(3)*(P(1)/P(R))**.5
      C=30.175*EXP(-3019.64/T)*P(2)*P(1)/(P(2)
      1+7.81E+04*P(R))
      DT=DPCHO/(.5-A-C+.0751*DPCHO)
      DYMOLE(2)=DPCHO+VDOT/(TR*10.73)
      DYMOLE(4)=C*ABS(DT)/(TR*10.73)*VDOT
C
C
C      THIS PART IS FOR THE TRAPIZOIDAL RULE
C
      R=(A-B+C-.0751*DPCHO)
      R=R/5
      Z=-DPCHO/R
      IF(DT .LT. 0)Z=DPCHO/R
      IF(DYMOLE(2) .EQ. DPCHO)Z=.5*Z
      SUMZ=SUMZ+Z
C
C      FIND THE VALUES OF THE OTHER COMPONENTS
      DYMOLE(5)=-.0751/(.3333+.6667*N)*DYMOLE(2)
      ALPHA=DYMOLE(4)/(-DYMOLE(2))*N*2
      D=.9249-ALPHA
      IF(DT .LT. 0)D=-1.0751-ALPHA
      DYMOLE(1)=(.5*ALPHA+.1502-D)*DYMOLE(2)-F*DYMOLE(4)
      DYMOLE(3)=(.5*(-ALPHA)-D)*DYMOLE(2)
      DYMOLE(6)=0
      DYMOLE(7)=0
      DYMOLE(8)=(-.0751+D)*DYMOLE(2)
      IF(DT .LT. 0)DYMOLE(2)=-DYMOLE(2)
      SUM=0
      DO 30 J=1,NP1
      YIMOLE(J)=YIMOLE(J)+DYMOLE(J)
      IF(YIMOLE(3) .LT. 0)YIMOLE(3)=0
30  SUM=SUM+YIMOLE(J)
      VDOT=SUM*10.73*TR/PFT
C
C      FIND THE NEW PARTIAL PRESSURES
      DPCHO=DPCHO
      DO 40 J=1,NP1
      P(J)=YIMOLE(J)*10.73*TR/VDOT
      IF(YIMOLE(2) .LE. (YCHOEN-DPCHO))DPCHO=-.01
C
C      IS YMOLE(2) CONVERGING?
      ENCO=ABS(YIMOLE(2)-YCHOEN)
      IF(ENCO .GT. (-DPCHO/10.73/TR*1.01*VDOT))GO TO 20
      SUM=1=0

```

```

SUM2=0
DO 50 J=1,NP1
  STDV(J)=Y1*MOLE(J)*.359
  WTP1(J)=Y1*MOLE(J)*FLOAT(MOLWT(2,J))
  SUM1=SUM1+STDV(J)
  SUM2=SUM2+WTP1(J)
50 Y1(J)=Y1*MOLE(J)/SUM
  HTVALF=STDV(1)*.424+STDV(2)*.322+STDV(4)*HTVAL1+STDV(5)*HTVAL2
  P1=SUM
  TSCF=SUM1+STDV(8)
  TWTP1=SUM2
  MIP=TWTP1/P1
  VDOTL=VDOT
  SUMZ=SUMZ+.5*Z
C
C   PRINT THE FINAL VALUES OF THE COMPONENTS
  WRITE(6,151)
  DO 60 J=1,NP1
60  WRITE(6,152)COMP(2,J),MOLWT(2,J),Y1(J),Y1*MOLE(J),WTP1(J),
    1P(J),STDV(J)
  WRITE(6,164) P1,MIP,TWTP1
164 FORMAT(/5X,'TOTAL MOLES OF GAS PRODUCT STREAM -- P1',25X,'= ',F8.2
    1,1X,'MOLES'/5X,'AVERAGE MOLECULAR WEIGHT OF GAS STREAM -- MIP',19X
    2,1X,'FR,2,1X,'LBS/MOLE'/5X,'TOTAL MASS -- P1*MIP',44X,'= ',F8.2,1X,
    3'LBS')
  VDOTI=SUMZ*VDOTI
  WRITE(6,160)SUMZ
160 FORMAT(/5X,'THE RESIDENCE TIME IS ',E15.4,' SEC')
C
C   THIS DETERMINES THE SCALE FACTOR

  SCAL=.9637E07/(HTVALF)
  HTVALF=.9637E01
  WRITE(6,158) HTVALF,SCAL
158 FORMAT(5X,'SCALE FACTOR FOR CONVERTING COAL BASE 1000 LBS/DAY TO
    11000 LBS/HR COAL'/5X,'BASE ',F5.2,' BILLION BTUS PER HR. PLANT',T
    175,'= ',F15.2)
C
C   THIS PART DOES THE ENERGY BALANCE OVER THE
C   FISHER-TROPSCH REACTOR
  TM2=320
  TM3=TFT
  TM4=TCGC1
  TM5=TFT+9
  SUM1=0
  SUM2=0
  SUM3=0
  SUM4=0
  SUM5=0
  DO 70 J=1,NP1
  CHL=1,
  HTU8A(J)=YR(J)*H(COMP(2,J),TM4)
  HTU8B(J)=YR(J)*H(COMP(2,J),TM2)
  HTU9A(J)=YR(J)*H(COMP(2,J),TM3)
  CHL=N
  HTU9B(J)=Y1*MOLE(J)*H(COMP(2,J),TM3)
  HTU9C(J)=Y1*MOLE(J)*H(COMP(2,J),TM5)
  SUM1=SUM1+HTU8A(J)
  SUM2=SUM2+HTU8B(J)
  SUM3=SUM3+HTU9A(J)
  SUM4=SUM4+HTU9B(J)
  SUM5=SUM5+HTU9C(J)
70 CONTINUE
  SUM4=SUM4-RTU9B(4)
  SUM5=SUM5-RTU9C(4)
  HTU8B(4)=HTU8B(4)/Y1*MOLE(4)*(Y1*MOLE(4)-YR(4))+H('CH4 '
    1,TM3)*YR(4)
  HTU9C(4)=HTU9C(4)/Y1*MOLE(4)*(Y1*MOLE(4)-YR(4))+H('CH4 '
    1,TM5)*YR(4)

```

```

SUM4=SUM4+BTU9H(4)
SUM5=SUM5+BTU9C(4)
H9C=BTU9C(4)/Y1MOLEF(4)
TRA=SUM1
T8H=SUM2
T9A=SUM3
T9H=SUM4
T9C=SUM5
DH9A=T8H-TRA
HTLR=DH9A
DH9A=T9A-T8H
TOI=150.
HOILIN=H('OIL',1,TOI)
TOL=TM3-20.
HOLV=H('OIL',1,TOL)
OMOLE=DH9A/(HOLV-HOILIN)
OILLV=HOILIN+OMOLE+DH9A
OILV2=HOLV+OMOLE-DH9A
OILV3=OILV2/OMOLE
TEMP=0
CALL NEWTON(OILV3,250.,TEMP)
DH9IL=OILV2-HOILIN+OMOLE
W1=ABS(DH9IL)/(TCWS-TCW)
GW1=7.48*1/62.15

C
C
C
C
C
WRITE THE ENERGY BALANCE

PRINT THE ENERGY BALANCE FOR GAS FEED-OIL HEAT EXCHANGER

WRITE(6,100)
WRITE(6,200)
200 FORMAT(30X,'ENERGY BALANCE FOR THE FISCHER-TROPSCH REA
1CTOP'//)
WRITE(6,205)TM4
205 FORMAT(30X,'GAS FEED INTO HEAT EXCHANGER @',F7.2,'F'//)
WRITE(6,210)
210 FORMAT(13X,'MOLES',7X,'BTU/MOLE',12X,'BTUS'//)
CHL=1
DO 80 J=1,NP1
HH=H(COMP(2,J),TM4)
WRITE(6,215) COMP(2,J),YH(J),HH,BTU8A(J)
215 FORMAT(6X,A4,2X,F6.3,6X,F9.1,8X,F12.1)
80 CONTINUE
WRITE(6,220)TRA
220 FORMAT(5X,'TOTAL BTUS',54X,'=',F15.1,1X,'BTUS')
WRITE(6,230)TM2
230 FORMAT(//30X,'GAS FEED OUT OF HEAT EXCHANGER @',F7.2,'F'//)
WRITE(6,210)
DO 82 J=1,NP1
HH=H(COMP(2,J),TM2)
82 WRITE(6,215) COMP(2,J),YH(J),HH,BTU8H(J)
WRITE(6,220)T8H
WRITE(6,240)TOL,TEMP
240 FORMAT(//10X,'OIL ENERGY BALANCE',/5X,'OIL TEMPERATURE IN',
146X,'=',F7.2,'F',/5X,'OIL TEMPERATURE OUT',45X,'=',F7.2,'F')
WRITE(6,241)OMOLE
241 FORMAT(5X,'MOLES OF OIL USED',46X,'=',F12.1)
WRITE(6,245)TM3
245 FORMAT(//10X,'GAS FEED INTO F-1 REACTOR @',F7.2,'F'//)

```

```

WRITE(6,210)
DO 84 J=1,NP1
HH=H(COMP(2,J),TM3)
84 WRITE(6,215) COMP(2,J),Y8(J),HH,BTU9A(J)
WRITE(6,220)T9A
WRITE(6,250)TM5
250 FORMAT(/30X,'GASEOUS PRODUCT OUT OF RXTOR @',F8.2,'F'//)
WRITE(6,210)
CHI=N
DO 86 J=1,NP1
HH=H(COMP(2,J),TM5)
IF(COMP(2,J).EQ.'H2C')HH=H9C
86 WRITE(6,215) COMP(2,J),Y1MOLE(J),HH,BTU9C(J)
WRITE(6,220)T9C
WRITE(6,230)T01,T0L
WRITE(6,241)OMOLE
WRITE(6,270)OILLV
WRITE(6,411) DHOIL
411 FORMAT(/5X,'HEAT LOAD FOR COOLER',44X,'=',F15.1,1X,'BTUS')
WRITE(6,412) W1,GW1
412 FORMAT(/5X,'COOLING WATER REQUIREMENT FOR COOLER (85F)',22X,'=',
1 F15.1,1X,'LBS/1000 LBS COAL'/69X,'=',F15.1,1X,
2 'GAL/1000 LBS COAL')
RETURN
END

```

APPENDIX B

SIZING SUBROUTINE

SIZING SUBROUTINE

```

C      FISCHER-TROPSCH REACTOR
C
10      WRITE(6,140)
140     FORMAT(//5X,'FISCHER-TROPSCH REACTOR'//)
      HTLH=-HTLH*SCAL
      WRITE(6,141)HTLH
141     FORMAT(5X,'OIL TO GAS HEAT EXCHANGER',T71,'=',F15.
      S1,1X,'BTU/HR')
      NG=VDOUTL*SCAL/(210.329*1.74945)+.5
      DTGX=NG
      DH9A=-DH9A*SCAL
      WRITE(6,142)DH9A
142     FORMAT(5X,'OIL TO GAS HEAT EXCHANGER',T71,'=',
      SF15.1,1X,'BTU/HR')
      DH9L=-DH9L*SCAL
      WRITE(6,143)DH9L
143     FORMAT(5X,'OIL COOLER',T71,'=',F15.1,1X,'BTU/HR')
      VDOUTL=VDOUTL*SCAL
      DMOLE=DMOLE*SCAL
      GWL=GWL*SCAL/60
      WRITE(6,144)GWL
144     FORMAT(5X,'COOLING WATER REQUIRED FOR COOLER',T71,
      S1=' ',F15.1,1X,'GPM')
      RETN=1
      END
  
```


APPENDIX C
ECONOMICS SUBROUTINE

ECONOMICS SUBROUTINE

```

CPF(2) = .85                                00007980
CALL COMPS(NU,HP,CPF,TC,T1,TT)                00007990
CALL SUM7(NH,'PIPELINE COMPRESSOR            ') 00008000
CALL HRSPWR(HP)                                00008010
C ***** OVERHEAD - METHANATION ***** 00008020
CALL PSUM(SPTTC,SPTI1,SPTIT,'METHANATION      ') 00008030
10 CONTINUE
CALL WRIT('FISC REP TRUP SCH ')
C CALCULATE COST ESTIMATES FOR THE FISCHER TROPSCH REACTOR
C OTGX= OIL TO GAS HEAT EXCHANGER
C COILX= OIL COOLER
C FTRX= FISCHER TROPSCH REACTOR
C OILPMP=OIL PUMP
C H2OPMP= WATER PUMP
C COILX=OTGX
C FTRX=OTGX
C OILPMP=OTGX
C H2OPMP=OTGX
C SPTTC=0.
C SPTI1=0.
C SPTIT=0.
C*****OIL TO GAS HEATER*****
NH=OTGX
HL=HTL8
U=30.
T1=TOL-320.
T2=TEMP-100.
TP=1.
PST=315.
PSS=300.
CALL HXCG(NH,HL,U,T1,T2,TP,PST,PSS,TC,T1,TT)
NH=OTGX+1
CALL SUM7(NH,'OIL TO GAS HEAT EXCHANGER ')
CALL HTLD(HL)
C*****OIL COOLER*****
NH=COILX
HL=DRHIL
U=50.
T1=TEMP-115.
T2=65.
TP=1.
PST=300.
PSS=50.
CALL HXCG(NH,HL,U,T1,T2,TP,PST,PSS,TC,T1,TT)
NH=COILX+1
CALL SUM7(NH,'OIL COOLER')
CALL HTLD(HL)
C***** FISCHER TROPSCH REACTOR *****
NH= FTRX
I=(PFT+25.)*115.2/(17500.-.6*(PFT+25.))+.25
V=7721.*T/12.
TC1=V*.2044.*491.*2.*600./472.
C FIND COST OF CATALYST
TC2=200*2.00*.6*600./472.
TC1=TC1+TC2
C FIND COST OF CYCLOGES
NH=NH+2
PSL=1.
ACFC=VDDT./60
CL(1)=0.

```

```

CL(2)=2.
CL(3)=285.
PS=300.
CALL CYCL(NU,ACFC,PS,CL,0,TC,T1,TT,PSL)
TC1=TC1+TC*2.
T1=TFT-TUL
T2=TFT-150.
DTL=(T1-T2)/ALOG(T1/T2)
A=DH9A/(30*DTL)
TC=ABS(A)*11.5/NU*2.*780./489.
TC=TC+TC1
T1=TC*.25
TT=TC+T1
NU=NU/2+1
CALL SUM7(NU,'FISC HER TROP SCH RXTD R' 1)
D=9.6
CALL DIAMER(D)
C***** START UP HEATER *****
NU=COILX/3.+667
TC=3425*15.
T1=.25*TC
CALL SUM7(NU,'STAR TUP HEAT ER' 1)
C***** OIL PUMP *****
NU=OILPMP
EFF=.72
GPM=GMOLE/(.87*62.4)*228/3600*7.48
POP=300.
PF(1)=1.50
PF(2)=1.
PF(3)=1.
PF(4)=1.
PF(5)=1.
TP=2.
CALL WATPMP(NU,GPM,EFF,POP,PF,TP,HP,TC,T1,TT)
NU=OILPMP+1
CALL SUM7(NU,'OIL PUMP' 1)
CALL HRSPMR(HP)
C***** COOLING WATER PUMP *****
NU=H2OPMP
EFF=.90
GPM=Gw1
POP=50.
PF(1)=1.
PF(2)=1.
PF(3)=1.2
TP=2.
CALL WATPMP(NU,GPM,EFF,POP,PF,TP,HP,TC,T1,TT)
NU=H2OPMP+1
CALL SUM7(NU,'FISC HER TROP SCH WATE R PU MP' 1)
CALL HRSPMR(HP)
C***** OVERHEAD FISCHER-TROPSCH *****
CALL PSUM(SPTTC,SPTTI,SPTTI,'FISC HER TROP SCH REAC
1 TUR')
CALL OVHD
WRITE(6,102) X1TC,X1T1,XAFT,XAVTTC,XAC,XHP
102 FORMAT('1',10X,'SYSTEM CAPITAL COST',T40,F15.2/
5 11X,'SYSTEM INSTALLATION COST',T40,F15.2/
5 11X,'SYSTEM OVERHEAD COST',T40,F15.2/
5 11X,'TOTAL SYSTEM COST',T40,F15.2//
5 11X,'TOTAL ANNUAL COST',T40,F15.2/

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```

00000040
00000050
00000060
00000070
00000080
00000090

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